

# Amino-acid salts for CO<sub>2</sub> capture from flue gases

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## Abstract

Amino-acid salt solutions provide an interesting alternative to amine based solutions for CO<sub>2</sub> capture from flue gases. Their specific properties make them suitable for application in membrane gas absorption units, allowing compact equipment design and potentially leading to reductions in investment costs. A further advantage can be achieved by the interesting feature of several amino-acid salts that solid precipitates are produced as the CO<sub>2</sub> loading exceeds a certain value. Due to this phenomenon, the equilibrium CO<sub>2</sub> pressure remains constant when the CO<sub>2</sub>-loading of the solvent further increases, so that the driving force for absorption can be maintained at a high level even at high loadings. This significantly improves the absorber performance. Furthermore, the high loadings lead to reduced energy consumption during regeneration. The use of precipitating solvents requires some adaptations of the equipment design: the absorber should be able to handle slurries, and the adapted temperature profile during desorption requires the heat exchanger to be partly integrated into the stripper column. Results of a preliminary economic evaluation are presented. It is shown that the proposed technology has the potential to substantially decrease the investment costs and the energy consumption of the capture process. The excellent perspectives have resulted in further fundamental research to provide a firm basis for a novel capture process based on precipitating solvents.

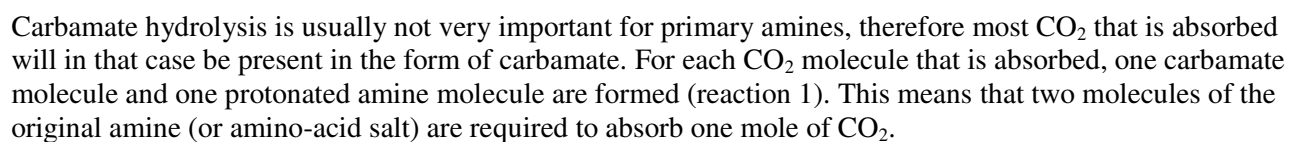
## 1. Introduction to the DECAB process

Post-combustion capture of CO<sub>2</sub> is one of the options considered for reduction of greenhouse gas emissions, since it can be integrated into existing power plants with relative ease. Solvent based technologies represent the leading capture technology being considered. Available solvents that are being investigated are almost exclusively based on aqueous amine solutions.

Amino-acid salt solutions provide an interesting alternative to conventional amine based solutions for CO<sub>2</sub> capture from flue gases. Distinguishing features are:

- Fast reaction kinetics
- High achievable cyclic loadings
- Good stability towards oxygen
- Favourable binding energy

Due to these advantages amino-acid salts have been marketed commercially in the past for removal of acid gas components. The range of Alkazid processes marketed by BASF is the best example of this [Kohl & Nielsen, 1996]. Their specific properties make amino-acid salts suitable for application in membrane gas absorption units, allowing compact equipment design and potentially leading to reductions in investment costs [Feron et al, 2002, Feron & ten Asbroek, 2004]. Their oxygen resistance has attracted further attention to investigate flue gas applications [Erga et al, 1995, Hook, 1997].



### 3. Effect of precipitation

At high  $\text{CO}_2$ -loadings of amino-acid solutions, precipitation occurs. There are two possible precipitates: the neutral amino acid (i.e. in fact the protonated amine from reaction 1), and a (bi)carbonate salt. In both cases, precipitation leads to increased absorption capacity, because the equilibrium of reaction 1) is shifted to the right. As a consequence, equilibrium pressures shift downward.

In figure 1 the equilibrium curve is shown for a 6 M amino acid-salt solution (denoted AmA) at  $40^\circ\text{C}$ . It is seen that at a  $\text{CO}_2$  loading of around 0.2 mole/mole precipitation starts, and the  $\text{CO}_2$  equilibrium pressure no further increases when the loading is further increased, up to a loading of about 0.3 mole/mole. From that point on, hardly any extra precipitation occurs and the  $\text{CO}_2$  pressure again rises with increasing loading.

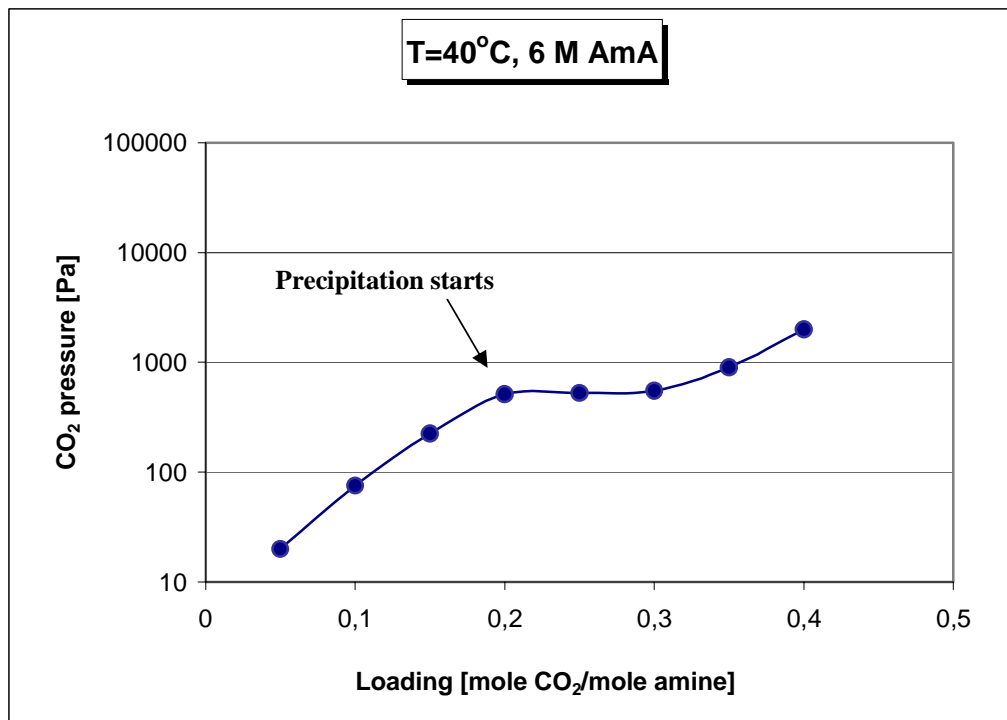


Figure 1: Equilibrium  $\text{CO}_2$  pressures vs. the loading during absorption

This behaviour opens up the possibility to significantly increase the total solvent loading at a specified  $\text{CO}_2$  pressure, offering great possibilities for cost reduction of capture processes. It is seen that at a typical flue gas  $\text{CO}_2$  pressure of 3 kPa, a rich loading of 0.4 mol/mol is achievable.

Just like “normal” amines, the loaded solvent containing the precipitate may be regenerated by increasing the temperature, driving off the  $\text{CO}_2$  and causing the precipitated amino acid to re-dissolve. As an example the equilibrium curves for a 6 M amino acid-salt solution at elevated temperatures are shown in figure 2. In experiments it has been shown that at a regeneration temperature of  $120^\circ\text{C}$ , a lean loading of 0.05 mol/mol is achievable, resulting in a cyclic loading of 0.35 mol/mol. This is significantly higher than MEA, which achieves typical cyclic loadings of 0.20-0.25 mol/mol.

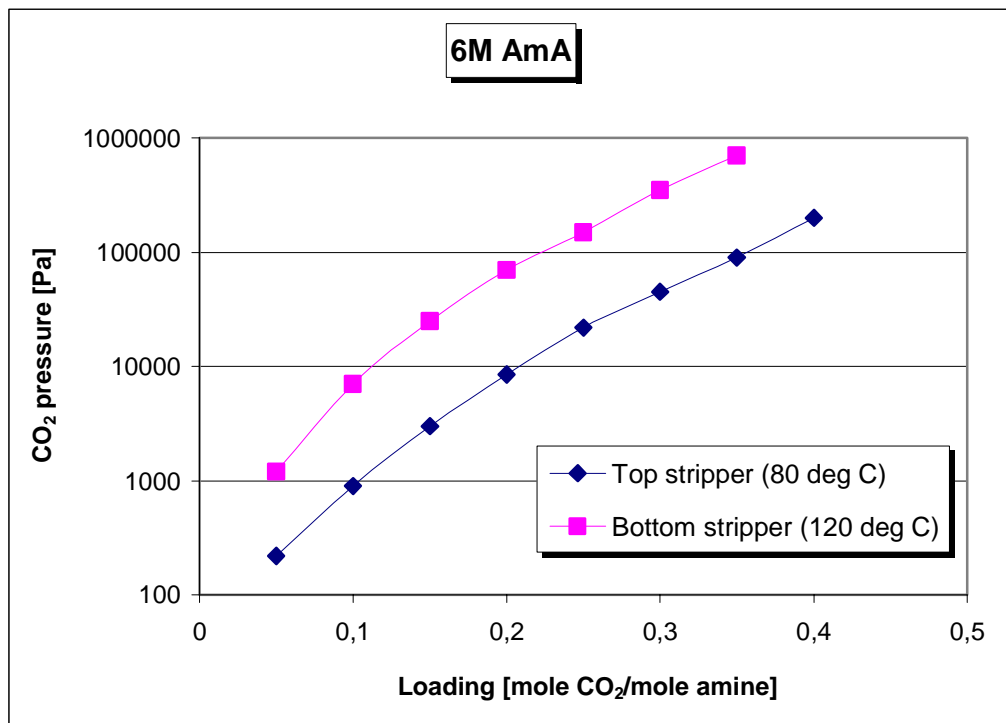


Figure 2: Equilibrium CO<sub>2</sub> pressures vs. the loading during desorption

#### 4. Process design

The use of precipitating solvents requires some adaptations of the equipment design. The absorber should be able to handle slurries, thus a spray column may be selected. The enhanced driving force for absorption due to precipitation, as well as the fast intrinsic reaction kinetics, compensate for the decrease in the specific surface area compared to packed columns. As a consequence, the absorber column will be of similar height as commonly used packed absorbers. Since expensive packing materials are left out this means a significant cost saving on investment. However, more detailed kinetic data and models are required to enable more accurate column sizing. Generally, due to the increased solvent loading, solvent recirculation rates can be decreased and equipment can be more compact.

Furthermore the adapted temperature profile during desorption requires the heat exchanger to be partly integrated into the stripper column. At a rich loading of 0.4 mol/mol, complete dissolution occurs when the loaded solvent is heated to 80°C. Above 80°C the solvent will release CO<sub>2</sub>, implicating that the loaded solvent can be fed as a clear liquid to the stripper at 80°C. However, complete regeneration requires the temperature at the bottom to be 120°C. This means that the temperature difference across the stripper amounts to 40°C, which is significantly higher than e.g. in a MEA based process, where the temperature difference is usually around 15°C. Therefore in the DECAB process, heat integration within the stripper is a must.

A schematic representation of the DECAB process is shown in figure 3.

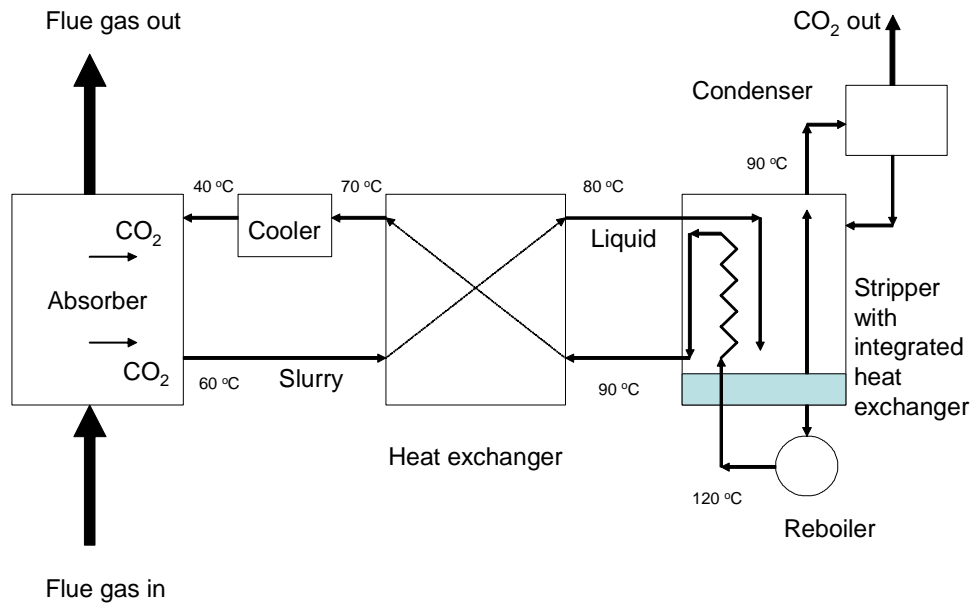


Figure 3: Schematic representation of the DECAB process

Typical process characteristics, as used in the techno-economic feasibility study (see section 5), are as follows:

- Solvent concentration: 6 M
- Lean loading: 0.05 mole CO<sub>2</sub>/mole amino-acid salt
- Rich loading: 0.40 mole CO<sub>2</sub>/mole amino-acid salt
- Hence cyclic loading: 92.4 kg CO<sub>2</sub>/m<sup>3</sup>
- CO<sub>2</sub>-desorption energy: 1.5 GJ/tonne CO<sub>2</sub> (including crystals dissolution heat )
- Stripper top temperature: 90°C hence low reflux (0.2 tonne steam/tonne CO<sub>2</sub>)
- Stripper bottom temperature: 120°C

## 5. Comparison with MEA-based capture process

In a techno-economic feasibility study, designs were made for the DECAB process as well as a conventional MEA based process, for capturing 90% of the CO<sub>2</sub> emission from a 500 MW pulverised coal fired power station and a 465 MW natural gas fired combined cycle (IEA base cases [IEA, 1992]). The following basis was taken for the evaluations (same for MEA-process and DECAB process):

- Annuity: 10% of overall investment
- Maintenance: 3% of overall investment
- Heat: 2 Euro/GJ
- Electricity: 0.04 Euro/kWh
- Cooling water: 0.05 Euro/m<sup>3</sup>
- Operating hours: 8000 per year

Results of the evaluations are given in tables 1-3.

*Table 1: Technical comparison of MEA and DECAB processes – consumption per ton CO<sub>2</sub> removal at a 500 MW pulverised coal fired power station*

	<b>MEA-based process</b>	<b>DECAB process</b>
Thermal energy	4.2 GJ	2.3 GJ
Electricity	69 kWh	41 kWh
Cooling water	73 m <sup>3</sup>	37 m <sup>3</sup>
Chemicals	1.0 kg	0.1 kg

*Table 2: Comparison of costs for 90% CO<sub>2</sub> removal at a 500 MW pulverised coal fired power station*

	<b>MEA-based process</b>	<b>DECAB process</b>
Fixed costs	6.6 euro/ton CO <sub>2</sub>	4.2 euro/ton CO <sub>2</sub>
Heat	8.4 euro/ton CO <sub>2</sub>	4.7 euro/ton CO <sub>2</sub>
Electricity	2.8 euro/ton CO <sub>2</sub>	1.6 euro/ton CO <sub>2</sub>
Cooling water	3.7 euro/ton CO <sub>2</sub>	1.8 euro/ton CO <sub>2</sub>
Chemicals	4.4 euro/ton CO <sub>2</sub>	1.0 euro/ton CO <sub>2</sub>
<b>Total</b>	<b>25 euro/ton CO<sub>2</sub></b>	<b>13 euro/ton CO<sub>2</sub></b>
<b>Emission avoided costs</b>	<b>34 euro/ton CO<sub>2</sub></b>	<b>15 euro/ton CO<sub>2</sub></b>

*Table 3: Summary of economic assessment: costs per ton of CO<sub>2</sub> avoided*

	<b>MEA-based process</b>	<b>DECAB process</b>
Pulverized coal fired	32-36 euro/ton CO <sub>2</sub>	15-16 euro/ton CO <sub>2</sub>
Gas fired combined cycle	41-46 euro/ton CO <sub>2</sub>	22-23 euro/ton CO <sub>2</sub>

It is shown that the proposed technology has the potential to substantially decrease the investment costs and the energy consumption of the capture process. Clearly the assumptions will have to be confirmed in further studies. The excellent perspectives have resulted in further fundamental research to provide a firm basis for a novel capture process based on precipitating solvents

## 6. Conclusions and future work

Aqueous solutions of salts of amino-acids provide an excellent alternative to amines for CO<sub>2</sub> capture from flue gases. Some of them show excellent oxygen resistance, lower binding energies and fast reaction kinetics. Using the precipitation high cyclic loadings can be achieved, resulting in potentially cost-effective process designs. However, the features need to be confirmed in future work.

In the near future attention will be given to:

- Liquid-gas contact in spray column with formation of precipitates
- Other amino-acid salts with favourable precipitation characteristics
- Validation in small scale pilot plant
- Interaction with SO<sub>2</sub>
- Equilibrium, kinetic and transport data for precipitating solvents
- Improved process modelling
- Validation in large scale pilot plant

The work is being carried in cooperation with Twente University (Prof. G.F. Versteeg) within the framework of the Dutch CATO Project.

## Acknowledgements

Part of the work has been supported by SenterNovem, an agency of the Dutch Ministry of Economic Affairs.

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